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13. ABSTRACT *(Maximum 200 words)*

The growth of heterojunction internal photoemission detectors and multiple quantum well detectors for the far- infrared has been explored. Structures have been grown using ultra- high vacuum chemical vapor deposition and have been characterized with X- ray diffraction, SIMS, RBS, and photoluminescence. Infrared response has been observed in some structures. Characterization performed to date has permitted the identification of growth parameters for experiments which will be performed in the next year.

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Development of Germanium- Silicon Growth Technology

Annual Report
AFOSR Contract F49620-92-J-0155

February 1, 1992- January 31, 1993

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Pittsburgh, PA

Research Objectives

This research is directed at the development of techniques for the growth of infrared detector structures using germanium- silicon strained epitaxial layers. The growth technique being used is ultra- high vacuum chemical vapor deposition, which is a multiple- wafer growth technique capable of abrupt transitions in composition and doping.

Our work is directed at two types of infrared detector structures. The first is a heterojunction internal photoemission detector which has a very heavily doped p- type germanium- silicon absorbing layer in contact with a p- type silicon substrate. This device is a heterojunction analog of the silicide Schottky barrier detector which is widely used at present. The second detector type is the multiple- quantum well infrared detector. In both device structures the threshold wavelength is determined by germanium composition of the layers and other growth parameters.

In the following, we outline progress in the past year on the further development of UHV/ CVD growth technology for these applications. While most of the work in the past year has been on optical and electrical characterization of various structures, we have also fabricated and characterized a few detector structures. Many of the important questions concerning surface preparation, uniformity, growth rates, and defect levels have been answered in the past year. Consequently we expect the work in the following year to primarily focus on detector fabrication and characterization.

Status of the Research Effort

Multiple Quantum Well Infrared Detectors

Figure 1 (top) shows a multiple quantum well infrared detector structure, where the mechanism for detection is the excitation of holes from the quantum ground state in a germanium- silicon well. Growth of multiple quantum well infrared detectors are very challenging due to the requirements of abrupt transitions in composition and doping and also for high quality material. In addition, application in focal plane arrays imposes particularly stringent requirements on uniformity. We have examined all of these important issues in the past year. In particular, we have grown and performed materials characterization on doped quantum well structures suitable for detectors. These wafers are presently being fabricated into devices and will be characterized for infrared response in the next year. We outline below the work in the past year.

We first grew multiple quantum well structures which were doped in the barrier. The periodicity of the structures was verified by high resolution X-ray diffraction performed by M. Capano at Wright Laboratories (Figure 2). X- ray diffraction also yielded measurements of the average germanium fraction and the thickness. Compositional uniformity of multiple quantum well structures and thick epitaxial layers were also determined from this data. As anticipated, excellent uniformity across the wafer was obtained (± 2.5% across a 75 mm wafer). Photoluminesence measurements showed that (1) the material was of high quality due to the observation of no- phonon exciton recombination lines and (2) that a quantum confinement shift was observed as a function of well thickness. This work led to a number of publications including the first report of photoluminescence from doped (as opposed to undoped) germanium-silicon multiple quantum wells.

In the course of this work, it became apparent that the line widths we observed were greater than those reported by other researchers working on undoped quantum wells. We therefore became interested in determining whether the broader linewidths were an indication of well thickness fluctuations in our samples or instead were attributable to the doping. We therefore grew and characterized undoped multiple quantum well structures for comparison.

Photoluminescence characterization of these samples showed linewidths very similar to those reported by other workers, providing strong evidence that doping in the barrier was the cause of the broadened linewidth and that we have fluctuations in quantum well width are not a problem. Typical data is presented in Fig. 3.

In addition, measurements on these samples were used to contribute to the clarification of two major issues in the germanium- silicon research community; namely, the origin of the "broad peak" in MBE samples about 120 meV below the germanium- silicon band gap and the practicality of electroluminescence from germanium- silicon.

We were able to show that UHV/ CVD grown multiple quantum wells never exhibit the "broad peak" frequently observed in MBE- grown samples. Instead, either the no- phonon exciton recombination line is observed with its replicas, or (for thicker quantum wells) lines characteristic of dislocations are seen. The transition between quantum well and dislocation photoluminescence is shown in Fig. 3. Taking these results together with other work in the literature, it is now possible to convincingly associate the "broad peak" with germanium- rich platelets. These do not form readily during CVD growth at the same temperatures at which they form in MBE- grown material because the surface hydrogen reduces surface mobility. This is in agreement with the suggestion in our proposal that hydrogen coverage during growth would have important and beneficial effects during the growth of quantum well structures.

We also fabricated undoped multiple quantum well structures into pin diodes in order to examine the electroluminescence behavior. At that time two types of electroluminescence had been reported: electroluminescence similar to the "broad peak" observed in MBE- grown samples, and phonon- resolved electroluminescence which had been just reported by two groups using CVD- grown material.

We observed phonon- resolved electroluminescence at 77 K which correlates well with photoluminescence at the same temperature (Fig. 4). There were, however, some detailed differences from previous studies with respect to the temperature dependence and no- phonon line intensity compared to the substrate luminescence. We attribute these differences to varying device structures (mainly doping levels) leading to substantial differences in excitation of various emission processes. The emission efficiency can very likely be increased to a degree upon optimization of these parameters.

We have recently begun to grow and characterize multiple quantum well samples doped in the well, which are the most suitable for detector applications. Figure 5 shows a SIMS profile of a 20- well structure, showing (at least to SIMS resolution) that the dopant has been placed in the well region. We have also used X- ray diffraction and photoluminescence to characterize these samples. Portions of a wafer have been sent to W. Mitchel at Wright Laboratories for spectrally resolved photoconductivity measurements. As noted above, we are fabricating similar wafers into devices and will begin characterization in the near future.

Heterojunction Internal Photoemission Detectors

Figure 1 (bottom) shows the band diagram of a heterojunction internal photoemission detector. Our first detectors fabricated using exactly this structure showed nearly ohmic behavior, which we attributed to the presence of boron at the original growth interface. This would dope the silicon surface p+ making it impossible to obtain a rectifying junction. Interfacial boron is widely observed in MBE and CVD growth and has been attributed to a number of causes including atmospheric contaminants. While we plan to study solutions to this difficulty in the future, at present we are using a different detector structure to circumvent problems with interfacial boron.

Figure 6 (top) shows the structure presently under investigation. An undoped silicon layer approximately 500 Å in thickness separates the germanium- silicon absorbing layer from the boron spike. A very thin undoped germanium- silicon layer (≈ 50 Å check) separates the absorbing layer from the silicon. This spacer layer was included (because of our initial difficulty in obtaining rectifying contacts) to guarantee that no p dopant is present in the silicon layer. Figure 6 (bottom) shows the measured SIMS profile for a structure with 10% germanium. The boron spike at the initial growth interface is also clearly visible. The boron concentration in the absorbing layer is about 8×10^{19} cm^{-3}. This is close to the maximum practical value with the 52 ppm diborane doping gas we used for this growth. We have since obtained a 500 ppm diborane gas bottle and are proceeding with growths which will have higher boron concentrations. We have also performed a series of growths at higher germanium fractions and have characterized the germanium fraction as a function of germane flow up to 32% germanium. We observed deviations from the linear relation between germanium fraction x and germane flow which was observed at lower x. We were able to fit new measurements well, however, by a model based on competitive adsorption of silane and germane.

A number of wafers have been fabricated into detector structures using a specially designed mask set. Despite difficulties with edge leakage and ohmic contacts to the substrate, we have succeeded in obtaining rectifying contacts in at least one case. Subsequent characterization both at Rome Laboratories and at Carnegie Mellon showed that this device in fact

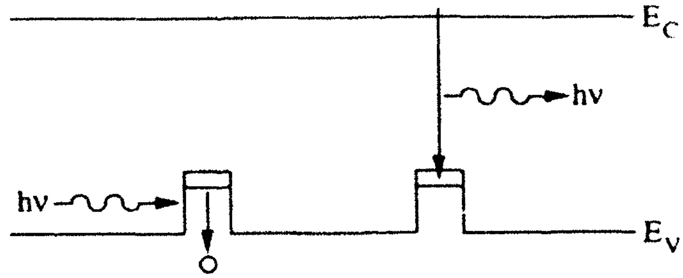
exhibited IR response at low temperatures. A plot of measured photoresponse as a function of wavelength is shown in Fig. 7. The threshold is at a higher energy than desired for 8- 12 μm detectors indicating a need for optimization of the germanium and boron concentrations.

The causes of our initial difficulties with non- recitifying junctions and substrate contacts now appear to be well understood. We will be proceeding in the next year with experiments on heavily- doped wafers in order to obtain a range of devices suitable for detailed characterization and comparison with other types of infrared detectors.

Summary

Two structures of interest for infrared detectors have been successfully grown during the past year. Multiple quantum well sample have yielded considerable information concerning the effect of surface hydrogen during growth and the nature of the band- to- band optical transitions. In addition, the utility of photoluminescence as a routine characterization tool of doped (as opposed to undoped) layers has been demonstrated.

Infrared response has been obtained from heterojunction internal photoemission infrared detectors, although the present structures are not by any means optimum. Difficulties associated with substrate preparation, ohmic contacts, and processing were encountered and solutions to these difficulties have been developed.



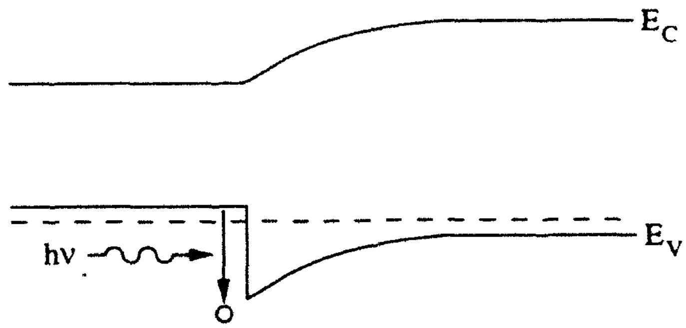


Fig. 1. Infrared detector structures (top) multiple quantum well detector and (bottom) heterojunction internal photoemission detector.

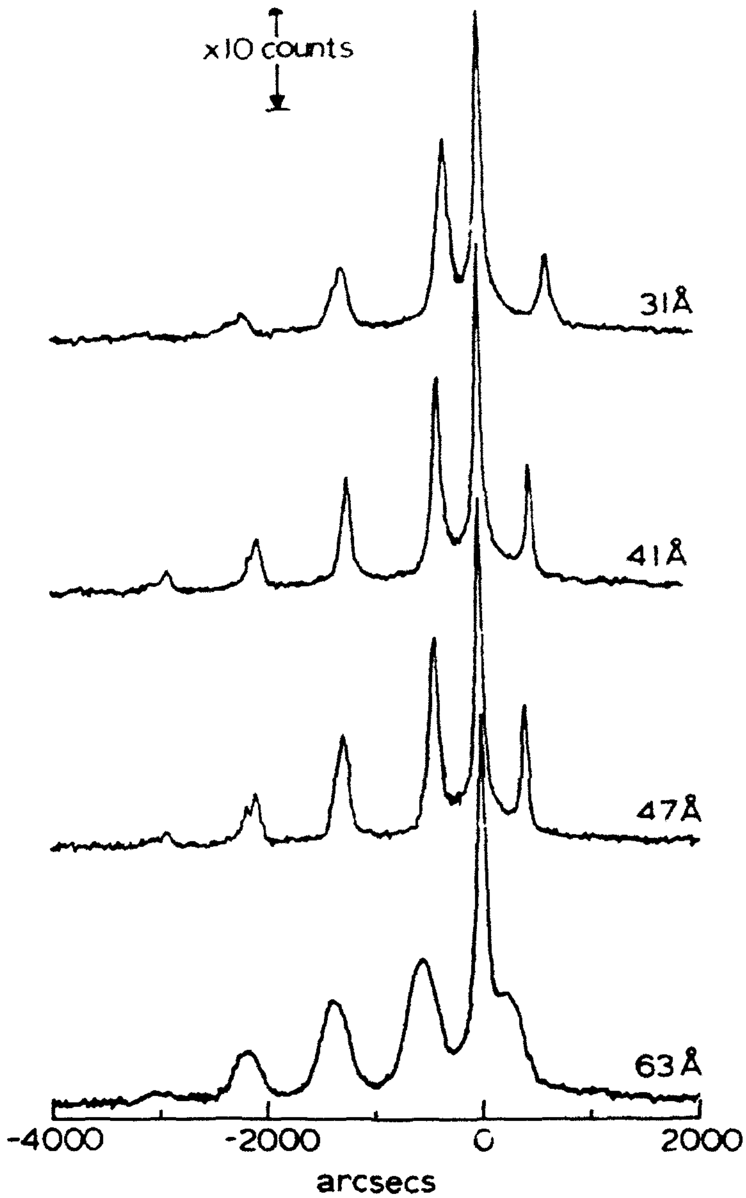


Fig. 2. High resolution X- ray diffraction spectra from multiple quantum well samples. The splitting between the zeroth order peak and the substrate peak is used to determine the average layer composition and the splitting between satellite peaks is used to calculate the multiple quantum well period. (Spectra taken by M.A. Capano, WPAFB).

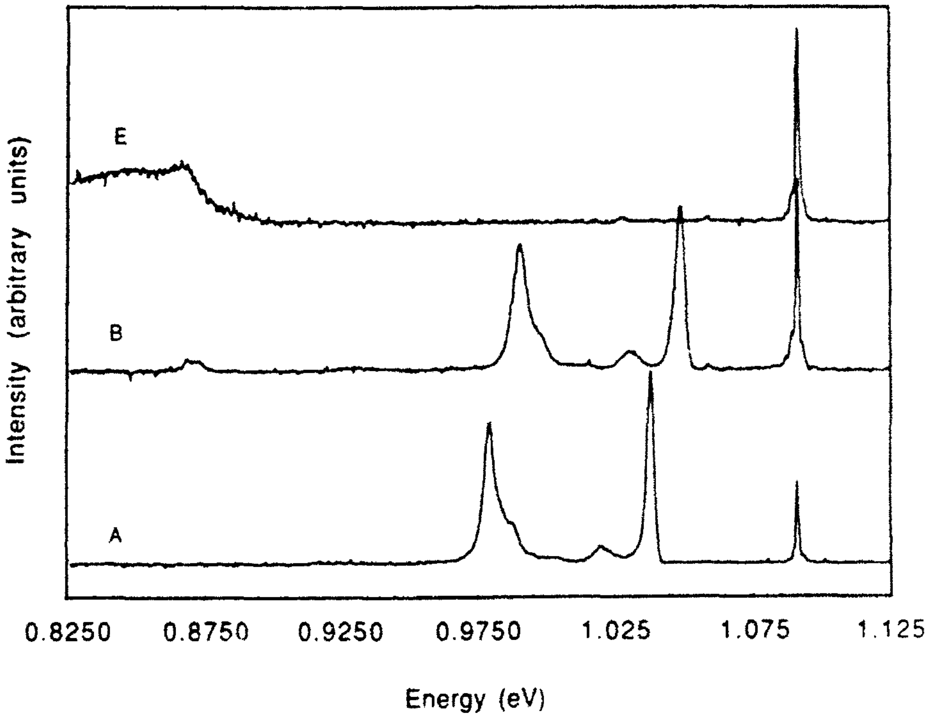


Fig. 3. Photoluminescence spectra of undoped multiple quantum well samples at 4.2K. Sample A: 56 Å well, x = 0.20; sample B: 44 Å well, x = 0.20; and sample E: ≈ 45 Å well, x = 0.32. Samples A and B show photoluminescence associated with silicon and sharp no phonon lines together with several phonon replicas. Sample E shows only silicon- related luminescence and a dislocation peak. Note that sample E has the highest germanium fraction.

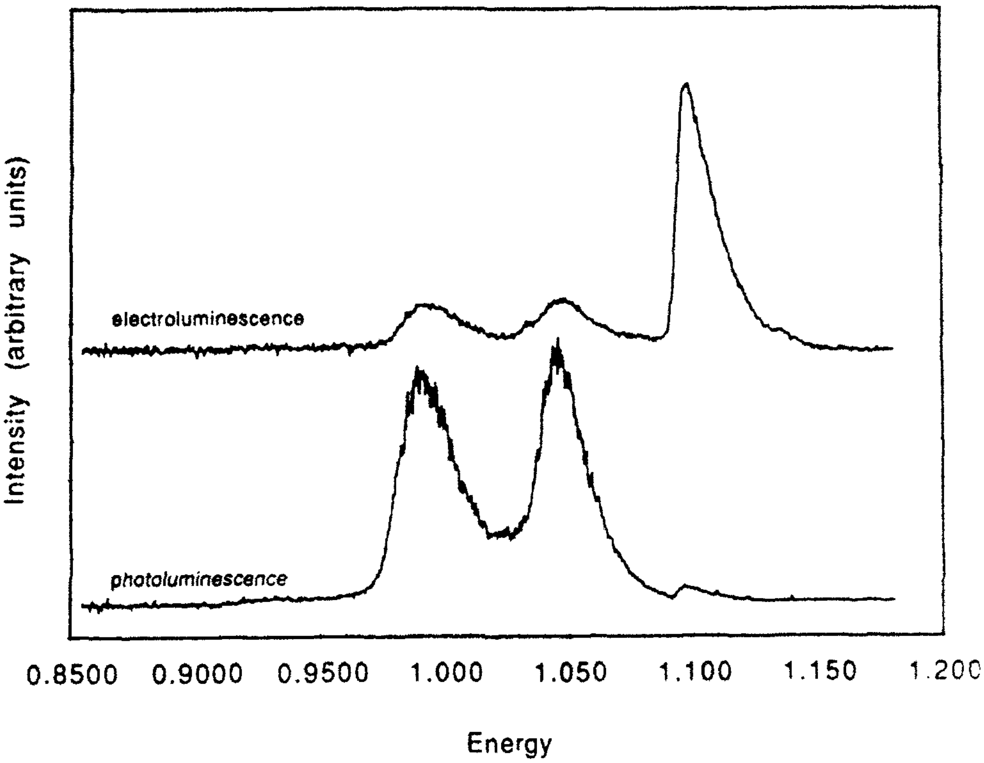


Fig. 4. Electroluminescence and photoluminescence spectra at 77 K from undoped multiple quantum well sample (56 Å wells, x = 0.20).

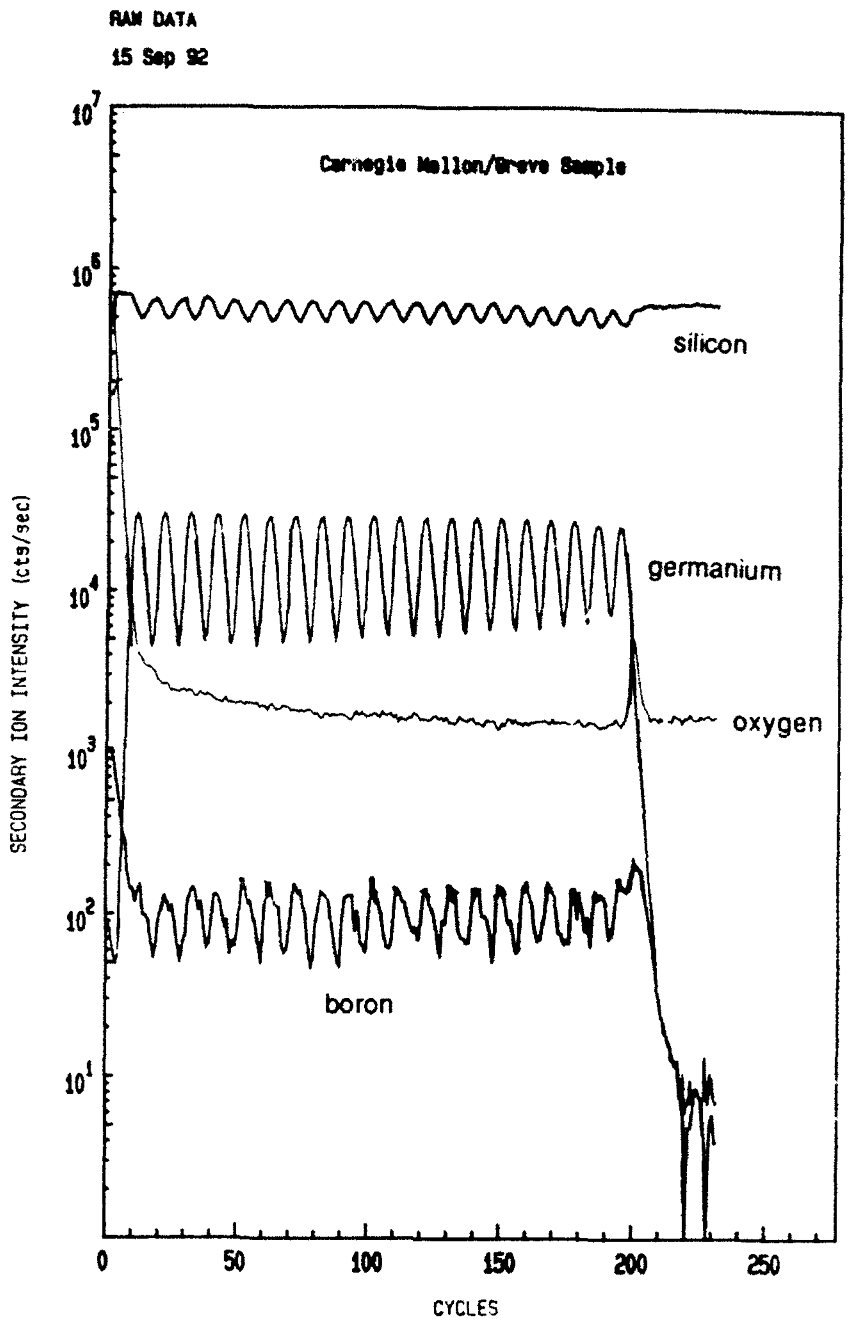


Fig. 5. SIMS profile (raw data) for sample with ≈ 60 Å wells, x = 0.20, with wells doped with boron. Within SIMS resolution, the boron peaks correspond with the well locations.

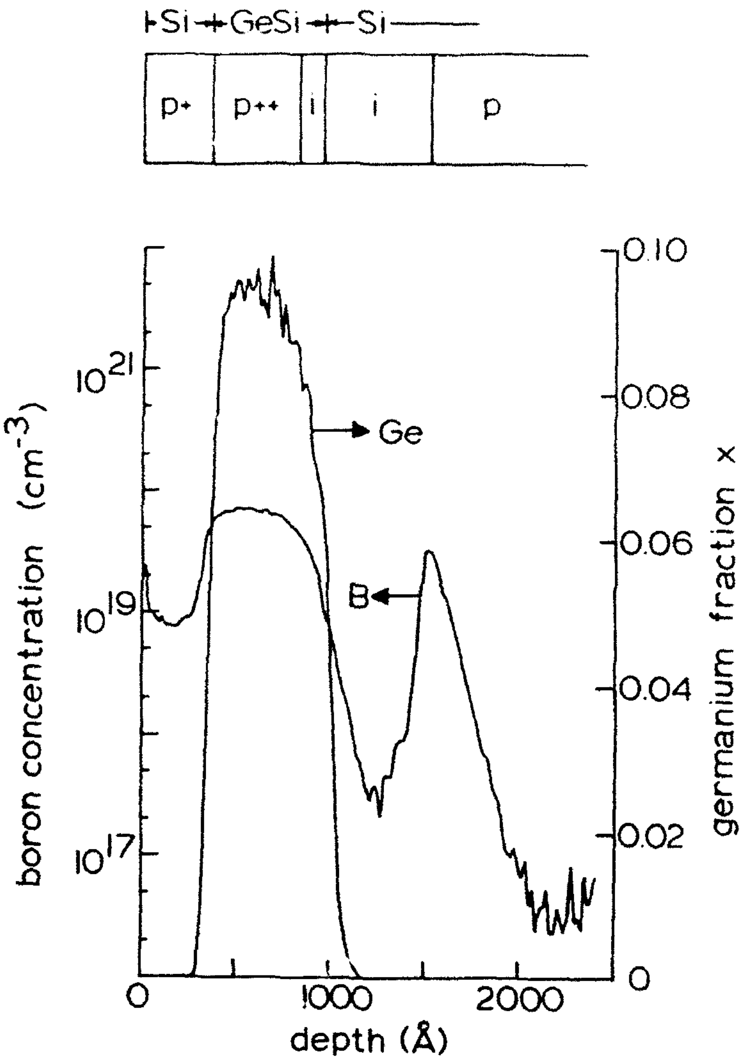


Fig. 6. Heterojunction internal photoemission detector structure (top) structure grown and (bottom) SIMS profile. The depletion region is terminated by the boron spike at the original wafer surface. The boron concentration in the absorbing layer is 8×10^{19} cm^{-3}.

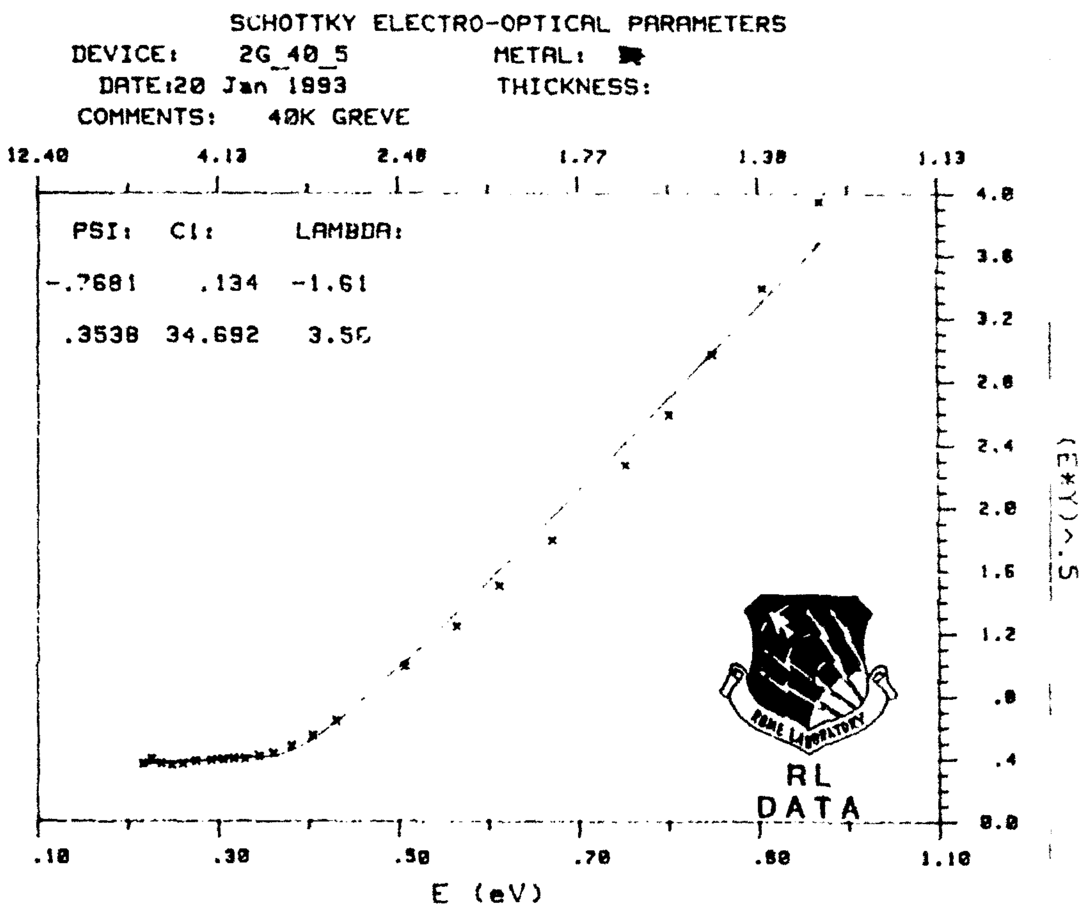


Fig. 7. Plot of (photoresponse)$^{1/2}$ power as a function of photon energy for heterojunction internal photoemission detector with $x = 0.20$. (Data taken by M.M. Chi, Rome Laboratory).

Publications

Review Article

"Growth of Epitaxial Germanium- Silicon Heterostructures by Chemical Vapor Deposition," D.W. Greve, (to be published in *Materials Science and Technology B*).

Journal Articles

"Incorporation of Boron into UHV/CVD- Grown Germanium-Silicon Epitaxial Layers," D.W. Greve and M. Racanelli, *J. Electron. Mater.* **21**, 593 (1992).

"Uniformity of Ge_xSi_{1-x} Epitaxial Layers Grown by Ultra-High Vacuum Chemical-Vapor Deposition," D.W. Greve, G. McLaughlin, M.A. Capano, and M. Racanelli, (to be published in *Appl. Phys. Lett.*).

"Photoluminescence and X-Ray Diffraction Study of Highly Uniform Si and Ge_xSi_{1-x} Epitaxial Layers" D.W. Greve, R. Misra, T.E. Schlesinger, and G. McLaughlin, *Thin Solid Films* 222, 46 (1992).

"Photoluminescence Characterization of UHV/ CVD Grown Multiquantum Wells," R. Misra, D.W. Greve, and T.E. Schlesinger, (to be published in *J. Electron. Mater.*).

"Characterization of Undoped Multiple Quantum Well Structures," R. Misra, R. Strong, D.W. Greve, and T.E. Schlesinger, (to be published in *J. Vac. Sci. Technol.*).

Conference Proceedings

"Kinetics of Thermal Cleaning for Silicon and Germanium-Silicon Epitaxy," M. Racanelli and D.W. Greve, *Proc. Second. Int'l. Symposium on Cleaning Technology in Semiconductor Device Manufacturing*, pp. 461-468, (The Electrochemical Society, Pennington, NJ, 1992).

"Comparison of Mesa-Etched and Ion-Implanted Ge_xSi_{1-x} Heterojunction Bipolar Transistors," D.W. Greve and M. Racanelli, (to appear in *Proc. 1992 Spring MRS, Symposium on Defect Engineering in Semiconductor Growth, Processing, and Device Technology*).

"Growth and Characterization of Ge_xSi_{1-x} Multiple Quantum Well Structures," D.W. Greve, R. Misra, M.A. Capano, and T.E. Schlesinger, *Proc. 1992 Spring MRS, Symposium on Mechanisms of Epitaxial Growth*, pp. 365- 370, (Materials Research Society, Pittsburgh, PA, 1992).

"Electrical and Structural Properties of Cobalt Annealed on Silicon- Germanium Epilayers," G. Sarcona, F. Lin, M.K. Hatalis, A.F. Cserhati, E. Austin, and D.W. Greve, (to appear in *Proc. 1992 Fall MRS*).

Personnel

Faculty

D.W. Greve, Professor ECE, principal investigator
T.E. Schlesinger, Associate Prof. ECE, co- investigator

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Ramesh Misra
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Richard Strong
(M.S. student ECE, supported by this grant, US citizen)
Sanjay Vyas
(M.S. student MSE, supported by AASERT grant, US citizen)

Interactions

Wright Laboratory, WPAFB

M.A. Capano- high resolution X- ray diffraction
W. Mitchel- spectrally resolved photoconductivity

Air Force Institute of Technology

R.L. Hengehold- cathodoluminescence and UV- excited photoluminescence

Lehigh University

M.K. Hatalis- investigation of cobalt silicides

Jet Propulsion Laboratory

E. Fossum- heterojunction internal photoemission FET (integrated detector/ readout; supported by Caltech President's fund)

Papers at meetings (upcoming)

"Characterization of Doped GexSi1-x Multiple Quantum Well Structures for Far- IR Detectors," R. Misra, D.W. Greve, R. Strong, and T.E. Schlesinger, (Symposium on Infrared Detectors- Materials, Processing, and Devices, Spring 1993 MRS Meeting).*

"Kinetics of Epitaxial Layer Growth from Silane on (100) Silicon, D.W. Greve, (Symposium on Common Themes and Mechanisms of Epitaxial Growth, Spring 1993 MRS Meeting).*

"Polycrystalline Germanium- Silicon- Growth and Applications," D.W. Greve (invited paper, Integrated Processing for Micro- and Opto- Electronics, European MRS, May, 1993).

"UHV/ CVD Growth of Germanium- Silicon," D.W. Greve, R. Misra, R. Strong, and T.E. Schlesinger, (invited paper, American Vacuum Society Fall Meeting, Orlando, FL, November, 1993).

Papers at meetings (February 1, 1992 - January 31, 1993)

"Comparison of Mesa-Etched and Ion-Implanted Ge_xSi_{1-x} Heterojunction Bipolar Transistors," D.W. Greve and M. Racanelli, *1992 Spring MRS, Symposium on Defect Engineering in Semiconductor Growth, Processing, and Device Technology*, San Fransciso, CA.

"Thickness and Compositional Uniformity of Epitaxial Layers Grown by UHV/ CVD, M.A. Capano, D.W. Greve, and M. Racanelli, *1992 Spring MRS, Symposium on Mechanisms of Epitaxial Growth*, San Fransciso, CA.

"Growth and Characterization of Ge_xSi_{1-x} Multiple Quantum Well Structures," D.W. Greve, R. Misra, M.A. Capano, and T.E. Schlesinger, *1992 Spring MRS, Symposium on Mechanisms of Epitaxial Growth*, San Fransciso, CA.

"Photoluminescence Characterization of UHV/ CVD Grown Multiquantum Well Structures," R. Misra, D.W. Greve, and T.E. Schlesinger, *1992 Electronic Materials Conference*, Boston, MA.

"Characterization of Undoped Multiple Quantum Well Structures, " R. Misra, R. Strong, D.W. Greve, and T.E. Schlesinger, *1992 Fall Meeting of the American Vacuum Society*, Chicago, IL.

"Electrical and Structural Properties of Cobalt Annealed on Silicon- Germanium Epilayers," G. Sarcona, F. Lin, M.K. Hatalis, A.F. Cserhati, E. Austin, and D.W. Greve, *1992 Fall MRS*, Boston, MA.

"Photoluminescence and X- ray Diffraction Study of Highly Uniform Silicon and Ge_xSi_{1-x} Epitaxial Layers, invited paper, *1992 Spring E- MRS*, Strasbourg, France.

Seminars

"Growth and Characterization of Ge_xSi_{1-x} Multiple Quantum Well Structures," Wright Laboratory, Wright- Patterson AFB, October 30, 1992.

"Growth and Characterization of Ge_xSi_{1-x} Multiple Quantum Well Structures," Department of Electrical Engineering, Notre Dame University, November 11, 1992.

"Applications of UHV/ CVD- Grown Silicon and Germanium- Silicon, Electronic Imaging Laboratory Seminar, Xerox Palo Alto Research Center, November 13, 1992.

Other

Session Co- Chair, Silicon - Based Heterostructures II- Quantum Devices, Fall 1992 AVS Meeting, Chicago, IL.

Inventions/ Patent Disclosures

None.